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Fabrication of Polydopamine with Silver Nanoparticles Coating on Titanium to Enhance Corrosion Resistance: An *In vitro* Analysis

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Abstract **Background:** Titanium and its alloys are widely used in biomedical implants due to their mechanical strength, corrosion resistance *and* biocompatibility. However, prolonged exposure to physiological environments such as Simulated Body Fluid (SBF) can lead to surface degradation and corrosion, compromising implant performance. **Objective:** This study aimed to enhance the corrosion resistance, bioactivity *and* antimicrobial properties of titanium implants by applying a polydopamine (PDA) coating embedded with silver nanoparticles (AgNPs). **Methods:** Titanium samples were first coated with PDA via self-polymerization, followed by silver nanoparticle deposition through sputtering. Surface characterization was carried out using energy-dispersive X-ray spectroscopy (EDX) and Fourier-transform infrared spectroscopy (FTIR). Electrochemical corrosion behavior was evaluated using potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS). **Results:** EDX confirmed the successful deposition of Ag on the PDA-coated titanium surface along with elements such as Al, K, O, Ca, C *and* Ti. FTIR spectra showed characteristic Ti-O-Ti and Ti-O bonds in uncoated samples. Potentiodynamic analysis revealed an improvement in corrosion resistance, with a positive shift in corrosion potential from -0.44 V to -0.29 V and a reduction in corrosion current density from 5.72×10^{-5} A/cm^2 to 2.68×10^{-6} A/cm^2. EIS demonstrated increased phase angles, indicating better barrier properties. Additionally, enhanced CaP deposition on the coated surface suggests improved biointegration. **Conclusion:** PDA-AgNP coatings significantly improve the corrosion resistance and bioactivity of titanium implants. This surface modification holds promise for extending implant longevity while promoting osseointegration and antimicrobial efficacy.

Key Words Dental Implants, Polydopamine, Silver nanoparticles, Corrosion, Resistance, Osseointegration

INTRODUCTION

Titanium and its alloys have been widely used in orthopedic and dental applications, serving as the primary material for external fixations, bone stabilization *and* artificial joints due to their excellent mechanical strength, corrosion resistance *and* biocompatibility [1]. In dentistry, titanium implants have demonstrated high survival rates and successful osseointegration over the decades, making them a preferred choice in implantology [2].

However, despite their advantages, titanium implants are susceptible to corrosion over time, which can lead to implant failure due to host rejection. Surface properties such as chemistry, roughness *and* interaction with biological tissues play a crucial role in determining the implant's long-term success. Corrosion can compromise the material's structural integrity, leading to fatigue failure and eventual degradation [3]. In the oral cavity, which functions as an electrochemical environment, corrosion can result in discoloration, pain *and* inflammatory conditions such as perioral stomatitis and gingivitis. Over time, these complications can contribute to peri-implantitis, negatively affecting implant longevity [4]. Although titanium naturally forms a protective oxide (TiO_2) layer, this barrier is not completely resistant to corrosive attacks. Once the TiO_2 layer is compromised, the underlying metal becomes vulnerable to degradation, similar to other base metal alloys. Studies have shown that marginal bone loss is more pronounced in titanium-sprayed implant surfaces due to the release of titanium ions, which inhibit hydroxyapatite formation and contribute to local osteolysis [5].

To mitigate these issues and prevent bacterial colonization, silver nanoparticles (AgNPs) have gained significant interest due to their strong antimicrobial properties. AgNPs exhibit bactericidal activity by interacting with microbial membranes, proteins *and* DNA, thereby preventing infection and promoting wound healing [6,7]. Additionally, AgNPs generate Reactive Oxygen Species (ROS), which further contribute to their antimicrobial effects. However, despite their benefits, AgNPs have shown limitations in biocompatibility, which necessitates modifications to improve their integration with biological tissues [8].

One promising approach to enhancing the biocompatibility and functionality of titanium implants is surface modification using polydopamine (PDA). PDA, a bioinspired polymer derived from dopamine, exhibits strong adhesive properties, high biocompatibility *and* hydrophilic characteristics [9]. It mimics the adhesive proteins secreted by mussels, allowing for stable bonding between implant surfaces and surrounding tissues. PDA not only enhances cellular adhesion and osteogenesis but also plays a crucial role in surface roughness and mechanical stability, making it an ideal candidate for implant coatings. Moreover, PDA degradation releases dopamine into the surrounding environment, which has been shown to regulate dopamine receptors on osteoblasts and osteoclasts, thereby influencing the bone remodeling process.

In addition to its intrinsic properties, PDA serves as an excellent intermediate layer for further surface modifications. It can facilitate the incorporation of functional materials such as nanoparticles, growth factors, peptides *and* hydrogels, enabling the development of "dual-modification" coatings that enhance both antibacterial and osteogenic functions [10]. Several *in vitro* and clinical studies have demonstrated the potential of PDA-coated surfaces in promoting bone cell attachment and proliferation while simultaneously providing an antibacterial effect when combined with AgNPs [11-13].

Given these advantages, this study aims to develop a PDA-AgNP composite coating on titanium implants using self-polymerization and evaluate its corrosion resistance. By integrating the biocompatibility of PDA with the antimicrobial properties of AgNPs, we seek to improve the longevity and performance of titanium-based implants, addressing key challenges in orthopedic and dental applications.

METHODS

Sample Preparation

Commercially pure titanium (Cp-Ti) metal sheets (2 mm thickness) as shown in Figure 1 were procured from M/s Uniforce Engineers, Chennai, India. The sheets were mechanically cut into dimensions of 15 mm×20 mm×2 mm (Figure 1). The Cp-Ti surface was ground sequentially using silica carbide paper with grit sizes ranging from 80 to 1000. Following mechanical polishing, the samples were ultrasonically cleaned in acetone and double-distilled water. The cleaned surfaces were then etched using Kroll's reagent (a mixture of 7.5 mL H_2O, 1.5 mL concentrated HNO_3 and 1.5 mL HF) for 10 seconds, rinsed with double-distilled water *and* air-dried at room temperature.

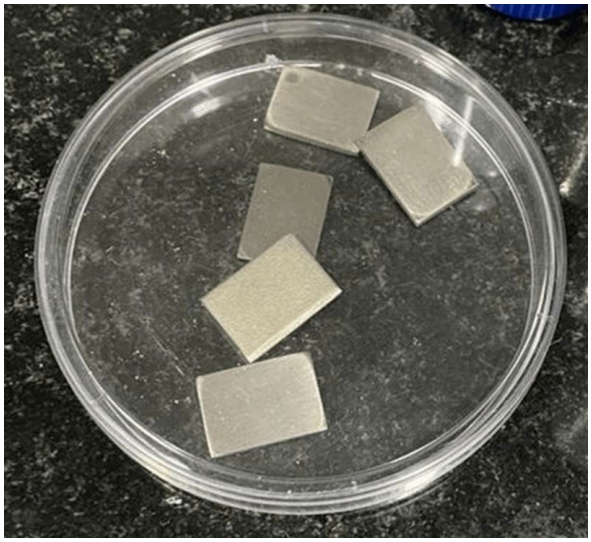

Figure 1: 15 mm×20 mm×2 mm pure titanium sheets

Polydopamine (PDA) Coating and Silver Nanoparticle (AgNP) Deposition

A polydopamine (PDA) layer was deposited on the titanium surface via self-polymerization. The PDA-coated samples were then subjected to silver nanoparticle (AgNP) deposition using a sputtering technique. The sputtering process was performed under vacuum conditions using the JEC-3000FC Auto Fine Coater, with a deposition time of 45 seconds at a current of 20 mA [14].

Characterization

The elemental composition of the coated samples were analyzed using energy-dispersive X-ray spectroscopy (EDX). Electrochemical performance was evaluated using potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) to assess corrosion resistance.Additionally, Scanning Electron Microscopy (SEM) was used to examine the surface morphology and biomineralization of PDA-AgNP after immersion in a biomimetic solution.

Electrochemical Corrosion Analysis of Bare and PDA-Coated Titanium

The corrosion behavior of both bare titanium and PDA-coated titanium was assessed using potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS). The experiments were conducted using a PGSTAT model 302 N electrochemical workstation (Metrohm Autolab B.V., Netherlands) controlled by NOVA 2.0 software. A three-electrode electrochemical cell was utilized, comprising a titanium sample (bare or PDA-coated) as the working electrode with an exposed surface area of 1 cm^2, a Saturated Calomel Electrode (SCE) as the reference electrode *and* a platinum foil as the counter electrode. To simulate physiological conditions, the corrosion tests were performed in Simulated Body Fluid (SBF), where the samples were immersed for one hour to establish a stable Open Circuit Potential (OCP) before testing [8].

Potentiodynamic polarization measurements were obtained by scanning the electrode potential from -1 V to +1 V relative to SCE at a scan rate of 1 mV/s. The corrosion potential (E_corr) and corrosion current density (i_corr) were determined using the Tafel extrapolation method.

Additionally, polarization resistance (R_p) was calculated using the Stern-Geary equation to evaluate the corrosion resistance of the samples.

Electrochemical Impedance Spectroscopy (EIS) was performed at OCP with an applied sinusoidal voltage of 10 mV across a frequency range of 0.01 Hz to 100 kHz. The resulting impedance data were analyzed using Nyquist and Bode plots to assess charge transfer resistance and surface stability. To further model the corrosion behavior of the samples, the obtained data were fitted using ZSimpWin software (Princeton Applied Research, USA) [15,16].

EDX Analysis

The elemental composition of PDA-AgNP was analyzed using Energy-Dispersive X-ray Spectroscopy (EDX). After undergoing the self-polymerization process, the PDA-AgNP samples were air-dried at a controlled room temperature of 37°C. To improve conductivity, the samples were coated with a thin layer of gold using a vacuum sputter coater (Polaron Q150RS, Hi-Tech Instruments, Malaysia). The EDX analysis was performed to determine the presence and distribution of key elements in the sample [17].

SEM Analysis for Biomineralization

The surface morphology and biomineralization of PDA-AgNP were examined using Scanning Electron Microscopy (SEM) after immersion in a biomimetic solution. The SEM images, captured at a magnification of 7500x and an operating voltage of 10 kV, revealed the deposition of a new layer on the PDA-AgNP surface. This layer appeared uniformly distributed, suggesting mineralization. The results indicate that polydopamine facilitates the nucleation of the calcium phosphate (CaP) layer, supporting its potential for bioactive applications and interaction with living tissues.

RESULTS

The experimental findings, presented in Figure 2, demonstrate that the PDA-COAT sample exhibited a more negative E_corr (-0.291 V) compared to the bare substrate (-0.088 V), indicating a shift towards a more stable corrosion potential. The significantly lower i_corr value (0.0278 µA/cm² for PDA-COAT vs. 0.1527 µA/cm² for BARE) confirms a reduced corrosion rate. Moreover, the R_p value of PDA-COAT (554.8 kΩ) was notably higher than that of BARE (26.57 kΩ), suggesting that the PDA coating significantly enhances corrosion resistance as shown in Table 1.

The potentiodynamic polarization analysis further supports that PDA-coated titanium exhibits superior corrosion resistance compared to bare titanium in Simulated Body Fluid (SBF). The lower corrosion current density (i_corr) observed for the PDA-coated sample suggests that the coating effectively reduces the corrosion rate by acting as a protective barrier against electrolyte penetration. Additionally, the more negative E_corr of the coated sample indicates a thermodynamic tendency towards corrosion. However, despite this shift, the significantly reduced i_corrimplies enhanced overall corrosion resistance.

Table 1: Potentiodynamic polarization data of the substrate (uncoated), PDA-AgNP coated samples

Sample	Ecorr (VSCE)	icorr (µA/cm2)	βa	-βc	Rp(kΩ)
Bare Titanium	-0.088	0.1527	3.1522	4.814	26.57
PDA-Coated Titanium	-0.291	0.0278	9.298	14.932	554.8

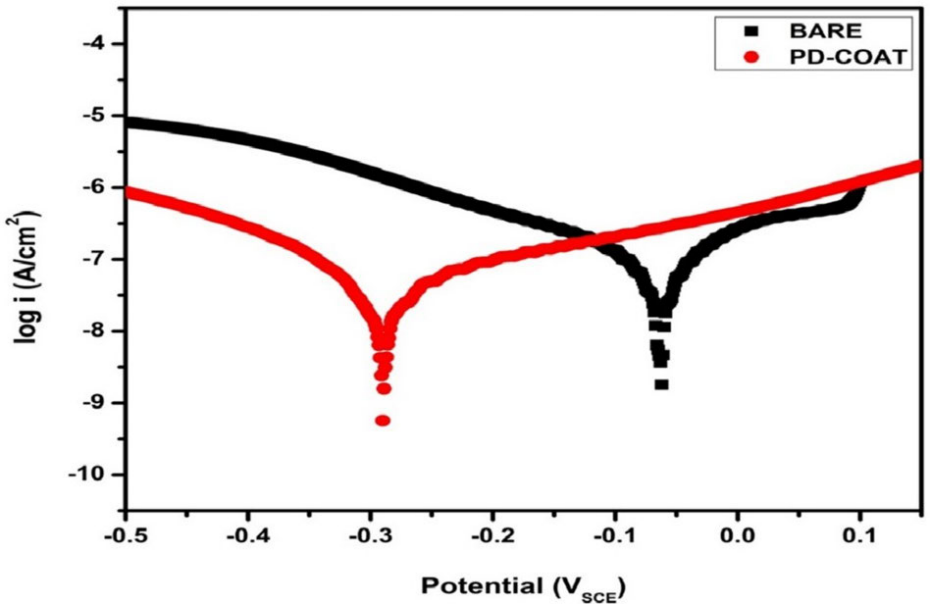

Figure 2: Potentiodynamic Polarization Curves of Bare and PDA-Coated Titanium in Simulated Body Fluid

Furthermore, the PDA-coated sample displays lower anodic and cathodic current densities, suggesting that the coating effectively inhibits both oxidation (metal dissolution) and reduction reactions. These findings confirm that PDA coating enhances the corrosion resistance of titanium, making it a promising surface modification for biomedical applications, where long-term durability and biocompatibility are crucial.

The Nyquist plot presented in Figure 3 compares the impedance behavior of bare titanium (BARE) and PDA-coated titanium (PD-COAT) in a Simulated Body Fluid (SBF) environment. The semicircle observed in the Nyquist plot represents the charge transfer resistance at the electrode/electrolyte interface, which is an indicator of corrosion resistance. The PDA-coated sample (represented by red circles) exhibits a significantly larger semicircle than the bare titanium (black squares), suggesting a higher charge transfer resistance. This indicates that the PDA coating enhances the protective barrier properties, reducing electrolyte penetration and minimizing corrosion reactions. The substantial increase in impedance for PD-COAT confirms its improved surface stability and corrosion resistance compared to bare titanium. These results suggest that PDA coating effectively enhances the electrochemical stability of titanium, making it a promising surface modification for biomedical applications requiring long-term durability in physiological environments.

The Figure 4 represents the Bode magnitude plot comparing the impedance (Z) of bare titanium and PDA-coated titanium as a function of frequency in a simulated

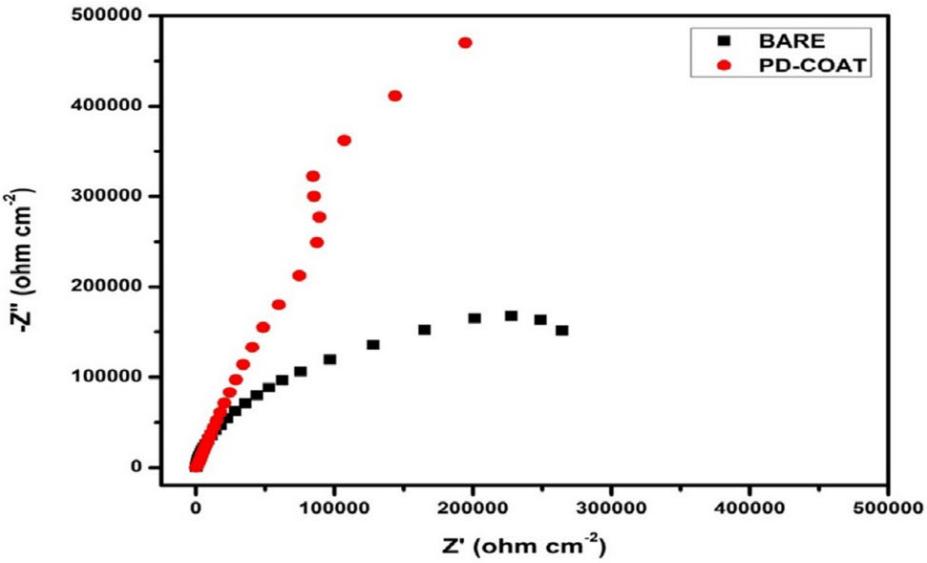

Figure 3: Nyquist Plot Comparing the Electrochemical Impedance of Bare and PDA-Coated Titanium in Simulated Body Fluid

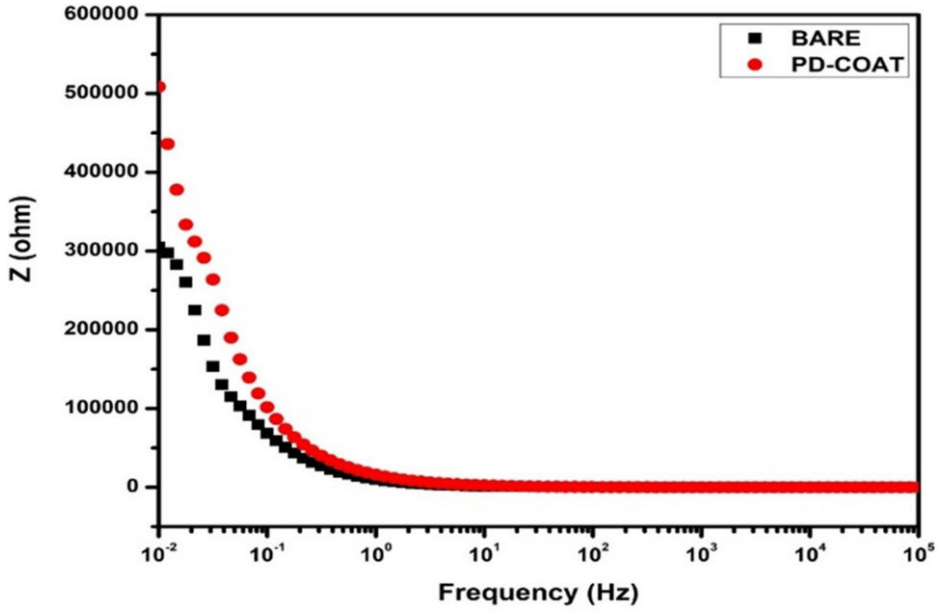

Figure 4: Bode Magnitude Plot Showing Impedance Variation of Bare and PDA-Coated Titanium in Simulated Body Fluid

body fluid environment. The red data points correspond to the PDA-coated sample, while the black data points represent the bare titanium. The PDA-coated titanium exhibits higher impedance (Z) across all frequency ranges compared to the bare titanium, indicating enhanced corrosion resistance. At low frequencies (left side of the graph), the impedance of the PDA-coated sample is significantly higher than that of the bare titanium, which suggests superior barrier protection against electrolyte penetration. Higher impedance at lower frequencies is typically associated with improved surface passivation and reduced charge transfer, confirming the effectiveness of the PDA coating in inhibiting corrosion.

The Bode phase angle plot as shown in Figure 5 reveals that the phase angle for PD-COAT remains closer to -80° over a broader frequency range, indicating a more capacitor-like behavior. This suggests that the polydopamine coating enhances the passive film properties of titanium, effectively reducing charge transfer processes and improving its resistance to bio-corrosion. Additionally, the shift of the phase peak towards lower frequencies in PD-COAT implies the presence of a more stable and thicker coating, which contributes to prolonged resistance against degradation, further reinforcing its protective capabilities.

The Energy-Dispersive X-ray Spectroscopy (EDX) analysis as illustrated in Figure 6 confirms the elemental composition of the PDA-AgNP-coated titanium surface. The high carbon (60.6%) and oxygen (31.7%) content indicate the presence of polydopamine (PDA) and possible oxide formation, suggesting successful surface modification.

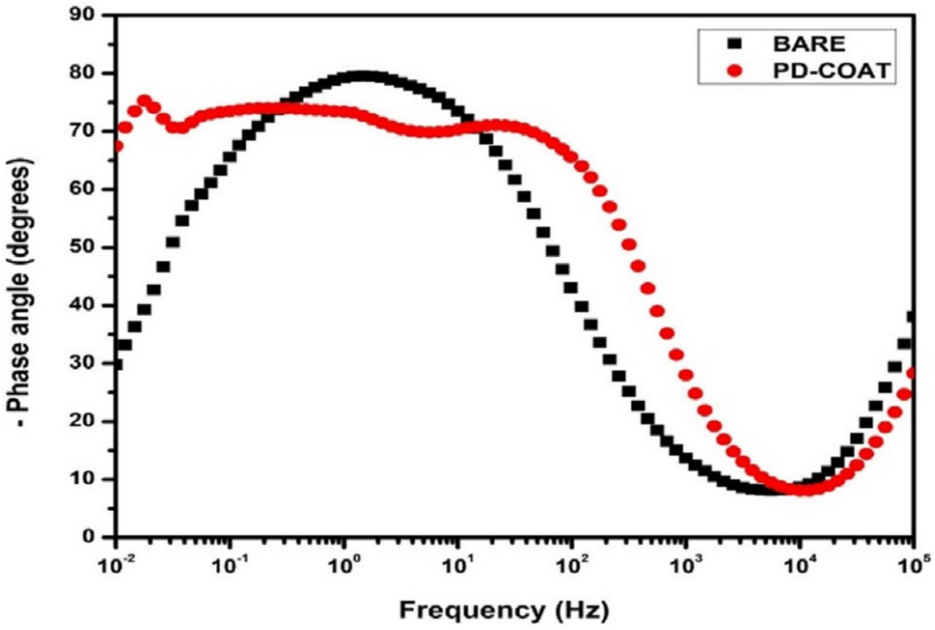

Figure 5: Bode Phase Angle Plot Comparing Bare Titanium and PDA coated Titanium

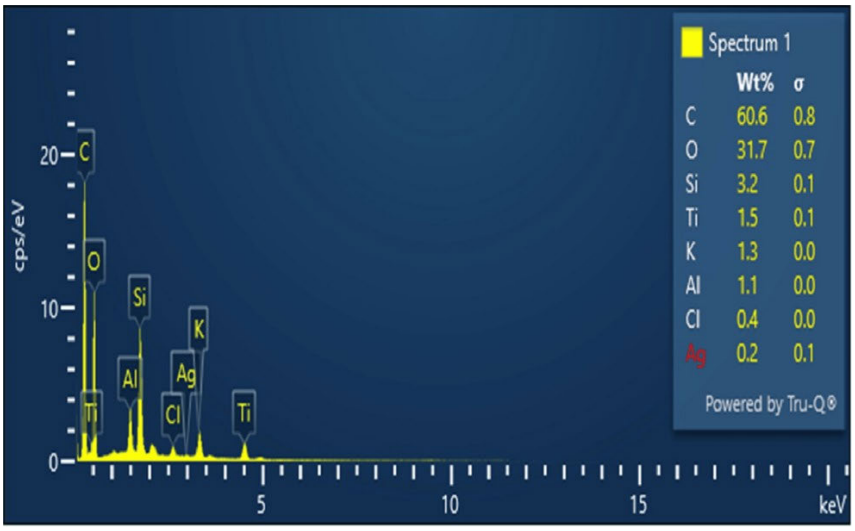

Figure 6: EDX Spectrum Confirming Elemental Composition of PDA-AgNP Coated Titanium Surface

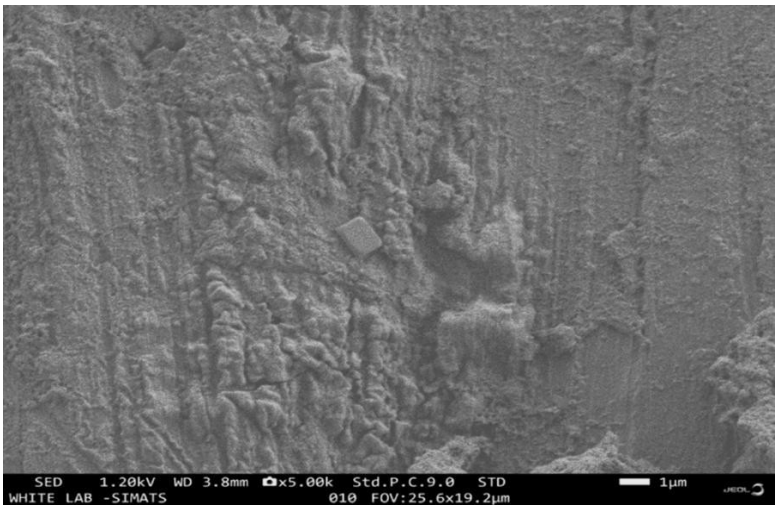

Figure 6: SEM Analysis of Biomineralized PDA-AgNP Surface After Immersion in Biomimetic Solution

A small amount of silver (0.2%) confirms the incorporation of Ag nanoparticles (AgNPs), which could contribute to antibacterial properties, although its low percentage suggests a thin or dispersed silver layer. The presence of titanium (1.5%) indicates that the underlying substrate is still detectable, implying that the coating is not excessively thick. Additionally, elements such as silicon (3.2%), potassium (1.3%), aluminum (1.1%) *and* chlorine (0.4%) suggest possible contaminants from processing or immersion in Simulated Body Fluid (SBF) during the biomineralization study.

The SEM analysis of the PDA-AgNP surface as illustrated in Figure 7 after immersion in a biomimetic solution revealed the successful deposition of a mineralized layer. The newly formed layer exhibited a uniform distribution, indicative of effective biomineralization. This suggests that polydopamine enhances the nucleation and growth of calcium phosphate (CaP), contributing to the bioactive potential of the material. The presence of this mineralized coating confirms the ability of PDA-AgNP to support interactions with biological environments, making it a promising candidate for biomedical applications, particularly in implant coatings and bone tissue engineering.

DISCUSSION

The findings of this study highlight the potential of polydopamine (PDA) and silver nanoparticle (AgNP) composite coatings in enhancing the corrosion resistance, bioactivity *and* antibacterial properties of titanium implants. The potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) results confirm that PDA coating improves electrochemical stability, as evidenced by the significant reduction in corrosion current density (i_corr) and the increase in polarization resistance (R_p). The corrosion potential (E_corr) of PDA-coated samples (-0.291 V) exhibited a nobler shift compared to the bare substrate (-0.088 V), reinforcing the superior corrosion resistance in Simulated Body Fluid (SBF). The i_corr of the uncoated substrate (0.1527 µA/cm^2) was substantially reduced to 0.0278 µA/cm^2 upon PDA incorporation, a result attributed to the partial filling of the substrate's compact pore walls by PDA, which acted as a barrier against corrosive ion penetration.

The SEM and EDX analyses further corroborate these results, showing the formation of a homogeneously distributed new layer on the PDA-AgNP surface. This layer suggests that PDA plays a pivotal role in triggering CaP layer nucleation and facilitating its deposition in a layer-by-layer manner, indicating that the PDA-AgNP coating possesses the capability to integrate with living tissue.

EIS analysis further substantiates the corrosion-resistant properties of PDA coatings. The semicircle diameter of PDA-coated samples exceeded that of the bare substrate, indicating improved impedance and superior corrosion resistance. The uniform PDA distribution acted as a physical barrier, impeding electrolyte migration toward the substrate. Compared to the substrate, PDA-coated samples demonstrated higher impedance and a phase angle shift, with values stabilizing at -65° in the low-frequency range. The formation of an anodic oxide layer contributed to an active barrier effect, reducing susceptibility to corrosive attack. The presence of two capacitive loops in PDA-coated samples, along with an increase in phase angle to -75° in the mid-frequency region and a stable low-frequency response, further signifies improved corrosion resistance [19,20].

Although direct mechanical testing such as scratch or nanoindentation was not performed in this study, the electrochemical findings serve as strong indirect evidence supporting the coating's adhesion and robustness. The broader and slightly deformed Nyquist semicircle observed in coated samples may suggest the presence of multiple time constants, indicating a dual barrier effect provided by both the PDA and AgNP layers. This is consistent with expected changes due to the modified surface chemistry. Future studies will include equivalent circuit modeling to

more accurately capture and explain these electrochemical behaviors. While EDX confirmed the presence of silver on the coated surface, detailed mapping was not included. However, the uniformly mineralized layer observed in post-immersion SEM suggests effective dispersion of AgNPs across the surface. In future work, EDX elemental mapping will be employed to visually confirm and quantify nanoparticle distribution.

The leaching behavior of silver nanoparticles was not quantified; however, the PDA matrix is known to provide a stable environment for nanoparticle immobilization, minimizing uncontrolled ion release. Sustained electrochemical performance in SBF over the study period suggests minimal leaching and good coating stability. Future investigations will focus on time-dependent release profiles and cytotoxicity studies to evaluate this further. The AgNP concentration used in this study was based on sputtering parameters derived from prior literature and optimized to balance functional performance and safety. The detected silver content (0.2%) in the EDX spectrum, combined with the absence of morphological changes or surface damage, suggests that the current level is both effective and biocompatible. However, detailed antibacterial efficacy tests and cytocompatibility assays will be included in follow-up work to identify the optimal loading threshold.

In addition to corrosion resistance, the PDA-AgNP coating also demonstrated bioactivity. The mineralized layer formed on the coated surface confirms its potential to promote favorable interactions with biological tissues, enhancing osseointegration. The antimicrobial contribution of silver complements this *but* its concentration must continue to be carefully controlled to ensure long-term biocompatibility. Despite these promising attributes, further evaluation is necessary to determine the long-term stability of the coating. While this *in vitro* study showed consistent electrochemical performance in SBF, future work will focus on time-lapse analysis to monitor coating integrity and performance in simulated physiological conditions over extended durations. Overall, the results underscore the significant potential of PDA-AgNP coatings as a multifunctional surface modification for titanium implants. With continued optimization of coating parameters and expanded *in vitro* and *in vivo* testing, this strategy holds promise for improving clinical outcomes in dental and orthopedic applications.

Clinical Significance

The PDA-AgNP coating presents a promising surface modification strategy for titanium implants, addressing critical challenges in implant longevity, biointegration *and* infection control. The significant enhancement in corrosion resistance, as demonstrated by reduced corrosion current density and increased polarization resistance, suggests improved durability in physiological environments, reducing the likelihood of implant degradation. Additionally, the coating facilitates calcium phosphate deposition, promoting superior osseointegration and bone-implant integration, which is essential for long-term stability. The antimicrobial properties of AgNPs further contribute to reducing infection risks, a major concern in orthopedic and dental implantology. However, optimizing AgNP concentration to balance antibacterial efficacy with biocompatibility remains essential. These findings support the clinical translation of PDA-AgNP coatings as a viable approach to enhancing implant performance, potentially leading to better patient outcomes and reduced implant failure rates.

CONCLUSIONS

This study highlights the significant potential of polydopamine-silver nanoparticle (PDA-AgNP) coatings in enhancing the corrosion resistance and bioactivity of titanium surfaces. The SEM and EDX analyses confirmed the formation of a uniform, well-distributed PDA-AgNP layer that facilitates CaP nucleation and deposition, indicating its potential for biointegration. Electrochemical studies revealed that PDA coatings substantially improve corrosion resistance, as evidenced by a significant reduction in corrosion current density and a nobler shift in corrosion potential. The enhanced impedance and formation of an anodic oxide barrier further corroborate the protective nature of PDA coatings against corrosive attacks in simulated body fluid (SBF). These findings align with previous research, reinforcing the superior electrochemical stability and biological functionality of PDA-based coatings. Overall, the results suggest that PDA-AgNP surface modifications could serve as a valuable strategy for improving the performance of titanium-based implants in dental applications.

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